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(71) Applicant: TOA NENRYO KOGYO KABUSHIKI KAISHA,
1-1 Hitotsubashi, 1-Chome Chiyoda-Ku, Tokyo 100 (JP)(43) Date of publication of application: 12.02.86
Bulletin 86/7(72) Inventor: Furuhashi, Hiroyuki, 1902-5, Ooaza Kamekubo
Ooi-machi, Iruma-gun Saitama-ken (JP)
Inventor: Yamamoto, Tadashi, 1902-5, Ooaza Kamekubo
Ooi-machi, Iruma-gun Saitama-ken (JP)
Inventor: Imai, Masaumi, 1902-5, Ooaza Kamekubo
Ooi-machi, Iruma-gun Saitama-ken (JP)
Inventor: Ueno, Hiroshi, 398-1, Ooaza Haneo
Namegawa-mura, Hiki-gun Saitama-ken (JP)

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(74) Representative: Northover, Robert Frank et al, ESSO
Chemical Limited Esso Chemical Research Centre P.O.
Box 1, Abingdon Oxfordshire, OX13 6BB (GB)

(54) Catalyst component for polymerization of olefins.

(57) A catalyst component for the polymerization of olefins
which is prepared by contacting (1) a contact reaction product
of (a) a metal oxide, (b) a dihydrocarbyl magnesium, and (c) a
halogen-containing alcohol held with (d) an electron-donating
compound, and (e) a titanium compound.

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CATALYST COMPONENT FOR POLYMERIZATION OF OLEFINS

2 This invention relates to a catalyst component for the
3 polymerization of olefins and, to the catalyst system comprising the
4 catalyst component, and to the process of polymerizing olefins,
5 especially olefins having 3 or more carbon atoms, in the presence of
6 the catalyst system.

7 **BACKGROUND OF THE INVENTION:**

8 Concerning Ziegler-Natta type catalysts which are effective
9 in polymerizing olefins, catalyst components having transition metals
10 deposited on a variety of carriers have been developed for the purpose
11 of improving catalyst activity per unit amount of catalyst or decreasing
12 residues originating in catalyst and persisting in produced
13 polymer.

14 A plurality of catalyst components using silica, alumina, and
15 other similar metal oxides as carriers for deposition of transition
16 metals have been proposed. Most of them are intended for polymeriza-
17 tion of ethylene. A very few of them are intended for polymeriza-
18 tion of alpha-olefins such as propylene.

19 As concerns catalyst compositions for the polymerization of
20 propylene, a catalyst component comprising a reaction product of a
21 metal oxide and a magnesium dialkoxide brought in contact with an
22 electron-donating compound and a tetravalent titanium halide (specifi-
23 cation of Japanese Patent Application Laid-open SHO 58[1973]-162,607)
24 and a catalyst component comprising a reaction product of an inorganic
25 oxide and a magnesium hydrocarbyl halide compound brought in contact
26 with a Lewis base compound and titanium tetrachloride (specification
27 of Japanese Patent Application Laid-open SHO 55[1980]-94,909) are
28 known to the art. These catalyst components, however, can hardly be
29 called satisfactory in terms of activity and stereoregularity.

30 Further, a catalyst component obtained by causing a
31 hydrocarbyloxysilane to react with a reaction product of a porous
32 carrier such as silica and an alkyl magnesium compound and subse-
33 quently causing a titanium halide compound to react upon the resultant
34 reaction product (specification of Japanese Patent Application Laid-
35 open SHO 57[1982]-153,006) and a catalyst component obtained by
36 causing an organic metal compound to react with a porous carrier,

1 causing a hydrocarbyl alcohol to react with the resultant reaction
2 product, and then causing a titanium halide compound to react with the
3 reaction product (specification of Japanese Patent Application
4 Laid-open SHO 57[1982]-200,408) have been proposed. These catalyst
5 components are intended for homopolymerization of ethylene or for
6 copolymerization of ethylene with other olefins. They are not
7 suitable for polymerization of alpha-olefins such as propylene.

8 DISCLOSURE OF THE INVENTION

9

10 It is an object of this invention to provide a catalyst
11 component which uses a metal oxide as a carrier and which is used for
12 homopolymerization of an olefin exhibiting high activity and high
13 stereoregularity, particularly an alpha-olefin such as propylene, and
14 for copolymerization of the aforementioned olefin with other olefins.
15 More particularly, in accordance with an object of this invention
16 there is provided a catalyst component which is prepared by contact-
17 ing a contact reaction product of a metal oxide, a dihydrocarbyl
18 magnesium, and a halogen-containing alcohol held in contact with an
19 electron-donating compound and a titanium compound.

20

23 To be specific, this invention essentially concerns a
24 catalyst component for the polymerization of olefins which is prepared
25 by contacting a contact reaction product of (1) (a) a metal oxide, (b)
26 a dihydrocarbyl magnesium, and (c) a halogen-containing alcohol
27 with (2) (d) an electron-donating compound and (e) a titanium
28 compound.

29 Raw materials for preparation of catalyst component

30 (A) Metal Oxide

The term "metal oxide" is used in this invention to refer
to oxides of elements in Groups II, III and IV in the
Periodic Table of Elements. Examples of the oxide
34 are B_2O_3 , MgO , Al_2O_3 , SiO_2 , CaO , TiO_2 , ZnO , ZrO_2 , SnO_2 , BaO , and
35 ThO_2 . Among other oxides enumerated above, B_2O_3 , MgO , Al_2O_3 , SiO_2 ,
36 TiO_2 , and ZrO_2 are more desirable selections, and SiO_2 is the most
37 desirable selection. Further, composite oxides including these metal
38 oxides are also usable. Examples of these composite oxides are

1 $\text{SiO}_2\text{-MgO}$, $\text{SiO}_2\text{-Al}_2\text{O}_3$, $\text{SiO}_2\text{-TiO}_2$, $\text{SiO}_2\text{-V}_2\text{O}_5$, $\text{SiO}_2\text{-Cr}_2\text{O}_3$, and
2 $\text{SiO}_2\text{-TiO}_2\text{-MgO}$.

3 The aforementioned metal oxides or composite oxides described
4 above are desirably anhydrous. The invention,
5 tolerates inclusion of a hydroxide in a very small amount normally
6 entrained in the metal oxide of the class under discussion. It also
7 tolerates inclusion therein of impurities to an extent incapable of
8 appreciably impairing the nature of metal oxide. Examples of the
9 impurities so tolerated are oxides, carbonates, sulfates, and nitrates
10 such as sodium oxide, potassium oxide, lithium oxide, sodium carbon-
11 ate, potassium carbonate, calcium carbonate, magnesium carbonate,
12 sodium sulfate, aluminum sulfate, barium sulfate, potassium nitrate,
13 magnesium nitrate, and aluminum nitrate.

14 Generally, the metal oxide of the foregoing description is
15 used in the form of powder. The size and shape of the individual
16 particles of this powder are desired to be suitably adjusted because
17 they often have bearing on the shape of the olefin polymer to be
18 produced. Prior to use, this metal oxide is fired at
19 appropriately high temperature to expel poisoning
20 substances and then held so as not to be exposed to the
21 atmosphere.

22 (B) Dihydrocarbyl Magnesium

23 The dihydrocarbyl magnesium to be used in the present inven-
24 tion (hereinafter referred to as "organic Mg") may be represented by the
25 general formula, RMgR' . In this formula, R and R', which can be the
same or different, preferably denote an alkyl, cycloakyl,
aryl, or aralkyl group of 1 to 20 carbon atoms.

28 Examples of the organic Mg are dimethyl magnesium (herein-
29 after "magnesium" will be abbreviated "Mg"), diethyl Mg, ethylmethyl
30 Mg, dipropyl Mg, diisopropyl Mg, ethylpropyl Mg, dibutyl Mg, diiso-
31 butyl Mg, di-sec-butyl Mg, di-tert-butyl Mg, butylethyl Mg, butyl-
32 propyl Mg, sec-butylethyl Mg, tert-butylisopropyl Mg, sec-butyl-tert-
33 butyl Mg, dipentyl Mg, diisopentyl Mg, ethylpentyl Mg, isopropylpentyl
34 Mg, sec-butylpentyl Mg, dihexyl Mg, ethylhexyl Mg, butylhexyl Mg,
35 tert-butylhexyl Mg, (2-ethylbutyl)ethyl Mg, (2,2-diethylbutyl)ethyl
36 Mg, diheptyl Mg, dioctyl Mg, di-2-ethylhexyl Mg, didecyl Mg, dicyclo-
37 hexyl Mg, cyclohexylethyl Mg, butylcyclohexyl Mg, di(methylcyclohexyl)
38 Mg, diphenyl Mg, ethylphenyl Mg, butylphenyl Mg, sec-butylphenyl Mg,

1 ditolyl Mg, ethyltolyl Mg, dixylyl Mg, dibenzyl Mg, benzyl-tert-butyl
2 Mg, diphenethyl Mg, and ethylphenethyl Mg.

3 The organic Mg may be a mixture of dihydrocarbyl
4 magnesium compounds or a complex, or a mixture with an
5 organic compound of other metal, such as a compound of
6 the general formula MR_n (wherein M denotes boron,)

7 beryllium, aluminum, or zinc, R denotes an alkyl, cycloalkyl, aryl, or
8 aralkyl group of 1 to 20 carbon atoms, and n denotes the valency of
9 the metal M). Examples of the organic compound of other
10 metals are triethyl aluminum, tributyl aluminum, triisobutyl aluminum
11 triphenyl aluminum, triethyl boron, tributyl boron, diethyl beryllium
12 diisobutyl beryllium, diethyl zinc, and dibutyl zinc.

13 In the aforementioned mixture or complex compound, the ratio
14 of the organic Mg to the organic compound of other metal generally is
15 such that the amount of the other metal is not more than 5 gram atoms
16 preferably not more than 2 gram atoms, per gram atom of magnesium.

17 (C) Halogen-containing Alcohol

18 The term "halogen-containing alcohol" as used in this
19 invention means a monohydric or polyhydric alcohol, thus
20 possessing one or more hydroxyl groups in the molecule
21 thereof having one or more hydrogen atoms thereof other
22 than the aforementioned hydroxyl group substituted with a
23 halogen atom. Examples of the halogen atom are chlorine,
24 bromine, iodine, and fluorine atom. Among the
25 halogen atoms cited above, the chlorine atom is particularly desirable.

26 Examples of the halogen-containing alcohol are 2-chloro-
27 ethanol, 1-chloro-2-propanol, 3-chloro-1-propanol, 1-chloro-2-methyl-
28 2-propanol, 4-chloro-1-butanol, 5-chloro-1-pentanol, 6-chloro-1-
29 hexanol, 3-chloro-1,2-propane diol, 2-chlorocyclohexanol, 4-chloro-
30 benzhydrol, (m,o,p)-chlorobenzyl alcohol, 4-chlorocatechol, 4-chloro-
31 (m,o)-cresol, 6-chloro-(m,o)-cresol, 4-chloro-3,5-dimethylphenol,
32 chlorohydroquinone, 2-benzyl-4-chlorophenol, 4-chloro-1-naphthol,
33 (m,o,p)-chlorophenol, p-chloro-alpha-methylbenzyl alcohol, 2-chloro-
34 4-phenylphenol, 6-chlorothimol, 4-chlororesorcin, 2-bromoethanol,
35 3-bromo-1-propanol, 1-bromo-2-propanol, 1-bromo-2-butanol, 2-bromo-
36 p-cresol, 1-bromo-2-naphthol, 6-bromo-2-naphthol, (m,o,p)-bromo-
37 phenol, 4-bromoresorcin, (m,o,p)-fluorophenol, p-iodophenol:
38 2,2-dichloroethanol, 2,3-dichloro-1-propanol, 1,3-dichloro-2-propanol,
39 3-chloro-1-(alpha-chloromethyl)-1-propanol, 2,3-dibromo-1-propanol,
40 1,3-dibromomono-2-propanol, 2,4-dibromophenol, 2,4-dibromo-1-naphtho-

1 2,2,2-trichloroethanol, 1,1,1-trichloro-2-propanol, β,β,β -trichloro-
2 tert-butanol, 2,3,4-trichlorophenol, 2,4,5-trichlorophenol, 2,4,6-
3 trichlorophenol, 2,4,6-tribromophenol, 2,3,5-tribromo-2-hydroxy
4 toluene, 2,3,5-tribromo-4-hydroxy toluene, 2,2,2-trifluoroethanol,
5 alpha,alpha,alpha-trifluoro-m-cresol, 2,4,6-triiodophenol: 2,3,4,6-
6 tetrachlorophenol, tetrachlorohydroquinone, tetrachloro-bis-phenol A,
7 tetrabromo-bis-phenol A, 2,2,3,3-tetrafluoro-1-propanol, 2,3,5,6-
8 tetrafluorophenol, and tetrafluororesorcin.

9 (D) Electron-donating Compound

10 Examples of the electron-donating compound are carboxylic
11 acids, carboxylic anhydrides, carboxylic esters, carboxylic halides,
12 alcohols, ethers, ketones, amines, amides, nitriles, aldehydes,
13 alcoholates, phosphorus, bismuth, and antimony compounds linked with
14 organic groups through the medium of carbon or oxygen atom, phos-
15 phamides, thioethers, thioesters, and carbonic esters. Among other
16 electron-donating compounds cited above, carboxylic acids, carboxylic
17 anhydrides, carboxylic esters, carboxylic halides, alcohols and ethers
18 are particularly desirable.

19 Concrete examples of the carboxylic acids are aliphatic mono-
20 carboxylic acids such as formic acid, acetic acid, propionic acid,
21 butyric acid, isobutyric acid, valeric acid, caproic acid, pivalic
22 acid, acrylic acid, methacrylic acid, and crotonic acid, aliphatic
23 dicarboxylic acids such as malonic acid, succinic acid, glutaric acid,
24 adipic acid, sebacic acid, maleic acid, and fumaric acid, aliphatic
25 oxycarboxylic acids such as tartaric acid, alicyclic carboxylic acids
26 such as cyclohexane monocarboxylic acids, cyclohexene monocarboxylic
27 acids, cis-1,2-cyclohexane dicarboxylic acids, and cis-4-methylcyclo-
28 hexane-1,2-dicarboxylic acids, aromatic monocarboxylic acids such as
29 benzoic acid, toluic acid, anisic acid, p-tert-butyl-benzoic acid,
30 naphtholic acid, and cinnamic acid, and aromatic poly carboxylic acids
31 such as phthalic acid, isophthalic acid, terephthalic acid, naphthalic
32 acid, trimellitic acid, hemimellitic acid, trimestic acid,
33 pyromellitic acid, and mellitic acid.

34 Concrete examples of carboxylic anhydrides are the anhydrides
35 of the carboxylic acids enumerated above.

36 Carboxylic esters are monoesters and polyesters of the car-
37 boxylic acids enumerated above. Concrete examples of such monoesters
38 and polyesters are butyl formate, ethyl acetate, butyl acetate, iso-

1 butyl isobutyrate, propyl pivalate, isobutyl pivalate, ethyl acrylate,
2 methyl methacrylate, ethyl methacrylate, isobutyl methacrylate,
3 diethyl malonate, diisobutyl malonate, diethyl succinate, dibutyl
4 succinate, diisobutyl succinate, diethyl glutarate, dibutyl glutarate,
5 diisobutyl glutarate, diisobutyl adipate, dibutyl sebacate, diisobutyl
6 sebacate, diethyl maleate, dibutyl maleate, diisobutyl maleate,
7 monomethyl fumarate, diethyl fumarate, diisobutyl fumarate, diethyl
8 tartrate, dibutyl tartrate, diisobutyl tartrate, ethyl cyclohexane-
9 carboxylates, methyl benzoate, ethyl benzoate, methyl p-toluate, ethyl
10 p-tert butylbenzoate, ethyl p-anisate, ethyl alpha-naphthoate, iso-
11 butyl alpha-naphthoate, ethyl cinnamate, monomethyl phthalate,
12 monobutyl phthalate, dibutyl phthalate, diisobutyl phthalate, dihexyl
13 phthalate, dioctyl phthalate, di-2-ethylhexyl phthalate, diallyl
14 phthalate, diphenyl phthalate, diethyl isophthalate, diisobutyl
15 isophthalate, diethyl terephthalate, dibutyl terephthalate, diethyl
16 naphthalate, dibutyl naphthalate, triethyl trimellate, tributyl
17 trimellate, tetramethyl pyromellate, tetraethyl pyromellate, and
18 tetrabutyl pyromellate.

19 Carboxylic halides are halides of the carboxylic acids
20 enumerated above. Concrete examples of such halides are acetic acid
21 chloride, acetic acid bromide, acetic acid iodide, propionic acid
22 chloride, butyric acid chloride, butyric acid bromide, butyric acid
23 iodide, pivalic acid chloride, pivalic acid bromide, acrylic acid
24 chloride, acrylic acid bromide, acrylic acid iodide, methacrylic acid
25 chloride, methacrylic acid bromide, methacrylic acid iodide, crotonic
26 acid chloride, maloic acid chloride, maloic acid bromide, succinic
27 acid chloride, succinic acid bromide, glutaric acid chloride, glutaric
28 acid bromide, adipic acid chloride, adipic acid bromide, sebatic acid
29 chloride, sebatic acid bromide, maleic acid chloride, maleic acid
30 bromide, fumaric acid chloride, fumaric acid bromide, tartaric acid
31 chloride, tartaric acid bromide, cyclohexane-carboxylic acid chloride
32 cyclohexane-carboxylic acid bromides, 1-cyclohexene-carboxylic acid
33 chloride, cis-4-methylcyclohexene-carboxylic acid chloride, cis-4-
34 methylcyclohexene-carboxylic acid bromide, benzoyl chloride, benzoyl
35 bromide, p-toluic acid chloride, p-toluic acid bromide, p-anisic acid
36 chloride, p-anisic acid bromide, alpha-naphthoic acid chloride,
37 cinnamic acid chloride, cinnamic acid bromide, phthalic acid
38 dichloride, phthalic acid dibromide, isophthalic acid dichloride,

1 isophthalic acid dibromide, terephthalic acid dichloride, and
2 naphthalic acid dichloride. Further monoalkylhalides of dicarboxylic
3 acids such as adipic acid monomethyl chloride, maleic acid monoethyl
4 chloride and maleic acid monomethyl chloride and phthalic acid butyl
5 chloride are also usable.

6 Alcohols are represented by the general formula ROH. In the
7 formula, R denotes an alkyl, alkenyl, cycloalkyl, aryl, or aralkyl
8 group of 1 to 12 carbon atoms. Concrete examples of such alcohols are
9 methanol, ethanol, propanol, isopropanol, butanol, isobutanol,
10 pentanol, hexanol, octanol, 2-ethylhexanol, cyclohexanol, benzyl
11 alcohol, allyl alcohol, phenol, cresol, xylene, ethyl phenol,
12 isopropyl phenol, p-tertiary butyl phenol, and n-octyl phenol. Ethers
13 are represented by the general formula ROR'. In the formula, R and R'
14 each denote an alkyl, alkenyl, cycloalkyl, aryl, or aralkyl group of 1
15 to 12 carbon atoms, providing that R and R' may be equal to or
16 different from each other. Concrete examples of such ethers are
17 diethyl ether, diisopropyl ether, dibutyl ether, diisobutyl ether,
18 diisoamyl ether, di-2-ethylhexyl ether, diallyl ether, ethylallyl
19 ether, butylallyl ether, diphenyl ether, anisol, and ethylphenyl
20 ether. Any of the compounds cited above as examples of halogen-
21 containing alcohols is also usable.

22 (E) Titanium Compound

23 Titanium compounds are divalent, trivalent, and tetravalent
24 titanium compounds. Concrete examples of such titanium compounds are
25 titanium tetrachloride, titanium tetrabromide, trichlorethoxy
26 titanium, trichlorobutoxy titanium, dichlorodiethoxy titanium,
27 dichlorodibutoxy titanium, dichlorodiphenoxy titanium, chlorotriethoxy
28 titanium, chlorotributoxy titanium, tetrabutoxy titanium, and titanium
29 trichloride. Among other titanium compounds enumerated above, such
30 tetravalent titanium halides such as titanium tetrachloride,
31 trichloroethoxy titanium, dichlorodibutoxy titanium, and dichloro-
32 diphenoxy titanium prove desirable and titanium tetrachloride proves
33 particularly desirable.

34 Method for Preparation of Catalyst Component

35 The catalyst component of the present invention is obtained
36 by contacting a reaction product comprising (a) a metal oxide
37 (hereinafter referred to as "A component"), the organic Mg
38 (hereinafter referred to as "B component"), and the halogen-containing

1 alcohol (hereinafter referred to as "C component") (b) with an
2 electron-donating compound (hereinafter referred to as "D component")
3 and a titanium compound (hereinafter referred to as "E component").

4 Contact of A Component, B Component, and C Component

5 The contact of A component, B component and C component is
6 effected by (1) a procedure of first establishing contact between A
7 component and B component and then introducing C component into
8 contact therewith, (2) a procedure of first establishing contact
9 between A component and C component and then introducing B component
10 into contact thereof, (3) a procedure of first establishing contact
11 between B component and C component and then introducing A component
12 into contact therewith, or (4) a procedure of establishing contact
13 among A component, B component and C component all at once.

14 The contact mentioned above, for example, is effected by
15 stirring the relevant components in the presence or absence of an
16 inactive medium or by mechanically comminuting the relevant component
17 jointly.

18 Examples of the inactive medium usable in the contact are
19 hydrocarbons such as pentane, hexane, heptane, octane, decane, cyclo-
20 hexane, benzene, toluene, and xylene and halides of hydrocarbons such
21 as 1,2-dichloroethane, 1,2-dichloropropane, carbon tetrachloride,
22 butyl chloride, isoamyl chloride, bromobenzene, and chlorotoluene.

23 The contact of A component, B component and C component is
24 generally carried out at a temperature of -20°C to +150°C for a period
25 of 0.1 to 100 hours. Where the contact entails evolution of heat,
26 there may be adopted a procedure of first mixing the components
27 gradually at a low temperature and, after all the components have been
28 wholly mixed, elevating the temperature and continuing the contact.
29 Further during the course of the contact of the components, the
30 individual components may be washed with the aforementioned inactive
31 medium. The proportions in which A component, B component, and C
32 component are used in the contact are such that the mol ratio B/A
33 falls in the range of 0.01 to 10, that of C/A in the range of 0.01 to
34 10, and that of C/B in the range of 0.1 to 20.

35 The solid product obtained by the contact of A component, B
36 component and C component (hereinafter referred to as "reaction
37 product I") is subjected to the subsequent contact. Optionally, the

1 reaction product I may be cleaned with a suitable cleaning agent such
2 as, for example, the aforementioned inactive medium.

3 Contact with D Component and E Component

4 The contact of the reaction product I with an electron-
5 donating (D component) and a titanium compound (E component) is
6 effected by (1) a procedure of first establishing contact between the
7 reaction product I and D component and then introducing E component
8 into contact therewith, (2) a procedure of first establishing contact
9 between the reaction product I and E component and then introducing D
10 component into contact therewith, or (3) a procedure of establishing
11 contact between D component and E component used jointly on one part
12 and the reaction product I on the other part.

13 The contact mentioned above is accomplished by mechanically
14 comminuting the relevant components jointly or stirring them in the
15 presence or absence of an inactive medium. It is more desirably
16 effected by stirring the relevant components in the presence or
17 absence of an inactive medium. As the inactive medium, any of the
18 aforementioned compounds can be used effectively.

19 When the contact of the reaction product I with D component
20 and C component is effected by their mechanical joint comminution, it
21 is effected generally at a temperature in the range of 0°C to 200°C
22 for a period of 0.1 to 100 hours. When the contact is carried out by
23 stirring, it is effected generally at a temperature of 0°C to 200°C
24 for a period of 0.5 to 20 hours. The amount of D component used in
25 this contact is in the range of 0.05 to 10 gram mols, preferably 0.01
26 to 1 gram mol, per gram atom of magnesium in the reaction product I.
27 The amount of E component used in the contact is above the level of
28 0.1 gram mol, preferably in the range of 1 to 50 gram mols, per gram
29 atom of magnesium in the reaction product I.

30 The contact between the reaction product I and E component
31 may be carried out twice or more. This contact can be effected by any
32 of the procedures mentioned above. In this case, the product from the
33 former contact may be cleaned with an inactive medium and the cleaned
34 product allowed to contact with a freshly added portion of E component
35 (in conjunction with the aforementioned medium).

36 Where the contact with E component is carried out in two or
37 more split steps, the reaction mixture under treatment may be allowed

1 to contact with an inactive hydrocarbon, halide of hydrocarbon, or
2 metal halide compound between the split steps of contact.

3 Examples of the inactive hydrocarbon usable for the contact
4 are aliphatic, alicyclic, and aromatic hydrocarbons. Concrete
5 examples of such hydrocarbons are n-hexane, methyl hexane, dimethyl
6 hexane, ethyl hexane, ethylmethyl pentane, n-heptane, methyl heptane,
7 trimethyl pentane, dimethyl heptane, ethyl heptane, trimethyl hexane,
8 trimethyl heptane, n-octane, methyl octane, dimethyl octane,
9 n-undecane, n-dodecane, n-tridecane, n-tetradecane, n-pentadecane,
10 n-hexadecane, n-octadecane, n-nonadecane, n-eicosane, cyclopentane,
11 cyclohexane, methyl cyclopentane, cycloheptane, dimethyl cyclopentane,
12 methyl cyclohexane, ethyl cyclopentane, dimethyl cyclohexane, ethyl
13 cyclohexane, cyclooctane, indane, n-butyl cyclohexane, isobutyl
14 cyclohexane, adamantane, benzene, toluene, xylene, ethylbenzene,
15 tetramethylbenzne, n-butylbenzene, isobutylbenzene, propyl toluene,
16 decalin, and tetralin.

17 Examples of the halide of hydrocarbon usable for the contact
18 are mono- and poly-halogen substitution products of saturated or
19 unsaturated aliphatic, alicyclic, and aromatic hydrocarbons. Concrete
20 examples of such compounds are aliphatic compounds such as methyl
21 chloride, methyl bromide, methyl iodide, methylene chloride, methylene
22 bromide, methylene iodide, chloroform, bromoform, iodoform, carbon
23 tetrachloride, carbon tetrabromide, carbon tetaiodide, ethyl
24 chloride, ethyl bromide, ethyl iodide, 1,2-dichloroethane, 1,2-
25 dibromo-ethane, 1,2-diido-ethane, methyl chloroform, methyl bromo-
26 form, methyl iodoform, 1,1,2-trichloro-ethylene, 1,1,2-tribromo-
27 ethylene, 1,1,2,2-tetrachloro-ethylene, pentachloro-ethane,
28 hexachloro-ethane, hexabromo-ethane, n-propyl chloride, 1,2-dichloro-
29 propane, hexachloro-propylene, octachloro-propane, decabromobutane,
30 and chlorinated paraffins, alicyclic compounds such as chlorocyclo-
31 propane, tetrachlorocyclo-pentane, hexachloro-pentane, and hexachloro-
32 cyclohexane, and aromatic compounds such as chlorobenzene, bromo-
33 benzene, o-dichlorobenzene, p-dichlorobenzene, hexachlorobenzene,
34 hexabromobenzene, benzotrichloride, and p-chlorobenzo-trichloride.

35 These compounds are such that one member of a mixture of two
36 or more members selected from the compounds enumerated above may be
37 advantageously used.

1 The metal halide compound is the halide of one element
2 selected from the class of elements of Group IIIa, Group IVa, and
3 Group Va in the Periodic Table of Elements (hereinafter referred to as
4 "metal halide"). Examples of the metal halide are chlorides,
5 fluorides, bromides, and iodides of B, Al, Ga, In, Tl, Si, Ge, Sn, Pb,
6 As, Sb, and Bi. Among other metal halides enumerated above, BCl_3 ,
7 BBr_3 , BI_3 , $AlCl_3$, $AlBr_3$, AlI_3 , $GaCl_3$, $GaBr_3$, $InCl_3$,
8 $TlCl_3$, $SiCl_4$, $SnCl_4$, $SbCl_5$, and SbF_5 prove particularly
9 desirable.

10 The contact of the reaction mixture optionally made with the
11 inactive hydrocarbon, halide of hydrocarbon, or metal halide (herein-
12 after referred to as "F component") between the two or more split
13 steps of contact made by the E component is carried out at a tempera-
14 ture in the range of 0° to 200°C for a period of 5 minutes to 20
15 hours, preferably at 20°C to 150°C for 10 minutes to 5 hours. When
16 the F component is a liquid substance, it is desired to be used in
17 such an amount that the reaction product I is obtained in an amount in
18 the range of 1 to 1,000 g per liter of the F component. When the F
19 component is a solid substance, this solid F component is desired to
20 be used as dissolved in another F component capable of dissolving the
21 solid F component. The amount of this solid F component is desired to
22 be such that the reaction product I is obtained in an amount in the
23 range of 0.01 to 100 g per g of the F component.

24 The mass of contact between the reaction product I with the
25 component E may be allowed to contact with the F component. This
26 contact can be carried out in the same manner as in the contact
27 optionally made by the use of the aforementioned F component.

28 The contact reaction product obtained as described above is
29 cleaned, when necessary, with hydrocarbon such as hexane, heptane,
30 octane, cyclohexane, benzene, toluene, or xylene, and then dried to
31 give birth to the catalyst component of the present invention.

32 The catalyst component of the present invention is formed of
33 particles having a specific surface area in the range of 10 to 1,000
34 m^3/g and a pore volume in the range of 0.5 to 5 cm^3/g as measured
35 by the BET method at the adsorption temperature of liquefied nitrogen
36 and possessing diameters so uniform as to be distributed in a narrow
37 range. As to percentage composition, this catalyst component
38 comprises 3 to 90% by weight of metal oxide, 1 to 25% by weight of

1 magnesium, 0.5 to 10% by weight of titanium, and 4 to 60% by weight of
2 chlorine.

3 Catalyst for the Polymerization of Olefins

4 The catalyst component of the present invention is used, as
5 combined with an organic compound of a metal selected from the class
6 of metals belonging to Groups I through III in the Periodic Table of
7 Elements, for catalyzing the homopolymerization of an olefin or the
8 copolymerization of the olefin with other olefins.

9 Organic Compound of Metal of Group I through Group III

10 Examples of the organic metal compounds usable in combination
11 with the catalyst component are organic compounds of lithium,
12 magnesium, calcium, zinc, and aluminum. Among other organic metal
13 compounds just mentioned, organic aluminum compounds prove
14 particularly desirable. The organic aluminum compounds usable herein
15 are represented by the general formula R_nAlX_{3-n} (wherein R denotes
16 an alkyl group or an aryl group, X denotes a halogen atom, an alkoxy
17 group or a hydrogen atom, and n denotes a desired number in the range
18 of $1 \leq n \leq 3$). Particularly desirable examples of the organic
19 aluminum compounds are alkyl aluminum compounds such as trialkyl
20 aluminum, dialkyl aluminum monohalide, monoalkyl aluminum dihalide,
21 alkyl aluminum sesquihalide, dialkyl aluminum monoalkoxide, and
22 dialkyl aluminum monohydride, respectively having 1 to 18 carbon
23 atoms, preferably 2 to 6 carbon atoms, and mixtures and complex
24 compounds thereof. Concrete examples of such organic aluminum
25 compounds are trialkyl aluminum such as trimethyl aluminum, triethyl
26 aluminum, tripropyl aluminum, triisobutyl aluminum, and trihexyl
27 aluminum, dialkyl aluminum monohalides such as dimethyl aluminum
28 chloride, diethyl aluminum chloride, diethyl aluminum bromide, diethyl
29 aluminum iodide, and diisobutyl aluminum chloride, monoalkyl aluminum
30 dihalides such as methyl aluminum dichloride, ethyl aluminum
31 dichloride, methyl aluminum dibromide, ethyl aluminum dibromide, ethyl
32 aluminum diiodide, and isobutyl aluminum dichloride, alkyl aluminum
33 sesquihalides such as ethyl aluminum sesquichloride, dialkyl aluminum
34 monoalkoxides such as dimethyl aluminum methoxide, diethyl aluminum
35 ethoxide, diethyl aluminum phenoxide, dipropyl aluminum ethoxide,
36 diisobutyl aluminum ethoxide, and diisobutyl aluminum phenoxide, and
37 dialkyl aluminum hydrides such as dimethyl aluminum hydride, diethyl
38 aluminum hydride, dipropyl aluminum hydride, and diisobutyl aluminum

1 hydride. Among other organic aluminum compounds enumerated above,
2 trialkyl aluminums, specifically triethyl aluminum, triisobutyl
3 aluminum, prove particularly desirable. The trialkyl aluminum can be
4 used in combination with other organic aluminum compounds such as
5 diethyl aluminum chloride, ethyl aluminum dichloride, ethyl aluminum
6 sesquichloride, diethyl aluminum ethoxide, or diethyl aluminum hydride
7 which is easily available commercially. These other organic aluminum
8 compounds may be used in the form of a mixture or complex compound.

9 Further, an organic aluminum compound having two or more
10 aluminum atoms linked through the medium of an oxygen atom or nitrogen
11 atom is also usable. Concrete examples of this organic aluminum
12 compound are $(C_2H_5)_2AlOAl(C_2H_5)_2$, $(C_4H_9)_2AlOAl(C_4H_9)_2$, and
13 $(C_2H_5)_2AlNAl(C_2H_5)_2$.

14 C_2H_5

15
16 Examples of organic compounds of metals other than aluminum
17 are diethyl magnesium, ethyl magnesium chloride, diethyl zinc and such
18 compounds as $LiAl(C_2H_5)_4$ and $LiAl(C_7H_{15})_4$.

19 The organic metal compound may be used independently or in
20 combination with an electron-donating compound. This electron-
21 donating compound may be any of the electron-donating compounds
22 employed in the preparation of the catalyst component described
23 above. Besides, organic silicon compounds capable of serving as
24 electron-donating compounds and electron-donating compounds containing
25 hetero atoms such as nitrogen, sulfur, oxygen, and phosphorus atoms are
26 also usable.

27 Concrete examples of organic silicon compounds are
28 tetramethoxy silane, tetraethoxy silane, tetrabutoxy silane, tetra-
29 isobutoxy silane, tetraphenoxy silane, tetra(p-methoxyphenoxy) silane,
30 tetrabenzylxy silane, methyl trimethoxy silane, methyl triethoxy
31 silane, methyl tributoxy silane, methyl triphenoxy silane, ethyl
32 triethoxy silane, ethyl triisobutoxy silane, ethyl triphenoxy silane,
33 butyl trimethoxy silane, butyl triethoxy silane, butyl triphenoxy
34 silane, isobutyl triisobutoxy silane, vinyl triethoxy silane, allyl
35 trimethoxy silane, phenyl trimethoxy silane, phenyl triethoxy silane,
36 benzyl triphenoxy silane, methyl triallyloxy silane, dimethyl
37 dimethoxy silane, dimethyl diethoxy silane, dimethyl diisopropoxy

1 silane, dimethyl dibutoxy silane, dimethyl dihexyloxy silane, dimethyl
2 diphenoxy silane, diethyl diethoxy silane, diethyl diisobutoxy silane,
3 diethyl diphenoxy silane, dibutyl disopropoxy silane, dibutyl
4 dibutoxy silane, dibutyl diphenoxy silane, diisobutyl diethoxy silane,
5 diisobutyl diisobutoxy silane, diphenyl dimethoxy silane, diphenyl
6 diethoxy silane, diphenyl dibutoxy silane, dibenzyl diethoxy silane,
7 divinyl diphenoxy silane, diallyl dipropoxy silane, diphenyl
8 diallyloxy silane, methylphenyl dimethoxy silane, and chlorophenyl
9 diethoxy silane.

10 Concrete examples of the electron-donating compound
11 containing a hetero atom are such nitrogen atom-containing compounds
12 as 2,2,6,6-tetramethyl piperidine, 2,6-dimethyl piperidine, 2,6-
13 diethyl piperidine, 2,6-diisopropyl piperidine, 2,2,5,5-tetramethyl
14 pyrrolidine, 2,5-dimethyl pyrrolidine, 2,5-diethyl pyrrolidine,
15 2,5-diisopropyl pyrrolidine, 2-methyl pyridine, 3-methyl pyridine,
16 4-methyl pyridine, 1,2,4-trimethyl piperidine, 2,5-dimethyl piper-
17 idine, methyl nicotinate, ethyl nicotinate, nicotinic acid amide,
18 benzoic acid amide, 2-methyl pyrrole, 2,5-dimethyl pyrrole, imidazole,
19 toluic acid amide, benzonitrile, acetonitrile, aniline, para-
20 toluidine, ortho-toluidine, meta-toluidine, triethyl amine, diethyl
21 amine, dibutyl amine, tetramethylene diamine, and tributyl amine, such
22 sulfur atom-containing compounds as thiophenol, thiophene, ethyl
23 2-thiophene carboxylate, ethyl 3-thiophene carboxylate, 2-methyl
24 thiophene, methyl mercaptan, ethyl mercaptan, isopropyl mercaptan,
25 butyl mercaptan, diethyl thioether, methyl benzenesulfonate, methyl
26 sulfite, and ethyl sulfite, such oxygen atom-containing compounds as
27 tetrahydrofuran, 2-methyl tetrahydrofuran, 3-methyl tetrahydrofuran,
28 dioxane, dimethyl ether, diethyl ether, dibutyl ether, diisoamyl
29 ether, diphenyl ether, anisole, acetophenone, acetone, methylethyl
30 ketone, acetyl acetone, ethyl 2-furalate, isoamyl 2-furalate, methyl
31 2-furalate, and propyl 2-furalate, and such phosphorus atom-containing
32 compounds as triphenyl phosphine, tributyl phosphine, triphenyl
33 phosphite, tribenzyl phosphite, diethyl phosphate, and diphenyl
34 phosphate.

35 These electron-donating compounds are such that two or more
36 members selected from the group of compounds enumerated above can be
37 used as a mixture. The electron-donating compound may be used at the

1 same time that the organic metal compound is used in combination with
2 the catalyst component or it may be used after it has been placed in
3 contact with the organic metal compound.

4 The amount of the organic metal compound to be used relative
5 to the catalyst component of the present invention falls generally in
6 the range of 1 to 2000 gram mols, preferably 20 to 500 gram mols, per
7 gram atom of titanium present in the catalyst component.

8 The proportions of the organic metal compound and the
9 electron-donating compound are such that the amount of the organic
10 metal compound falls in the range of 0.1 to 40 gram atoms, preferably
11 1 to 25 gram atoms, per mol of the electron-donating compound.

12 Polymerization of Olefins

13 The catalyst which comprises the catalyst component obtained
14 as described above and the organic metal compound (and the
15 electron-donating compound) is useful for catalyzing homopolymeriza-
16 tion of a monoolefin of 2 to 10 carbon atoms or copolymerization of
17 the monoolefin in combination with other monoolefins or diolefins of 3
18 to 10 carbon atoms. The catalyst exhibits an outstanding function,
19 particularly in catalyzing homopolymerization of an alpha-olefin such
20 as, for example, propylene, 1-butene, 4-methyl-1-pentene, or 1-hexene,
21 copolymerization of two such alpha-olefins and/or random and block
22 copolymerization of the alpha-olefin with ethylene.

23 The polymerization may be carried out in either the gaseous
24 phase or the liquid phase. When the polymerization is performed in
25 the liquid phase, it can be effected on a liquid monomer in an
26 inactive hydrocarbon such as normal butane, iso-butane, normal pen-
27 tane, iso-pentane, hexane, heptane, octane, cyclohexane, benzene,
28 toluene, or xylene. The polymerization temperature falls generally in
29 the range of -80°C to +150°C, preferably in the range of 40°C to
30 120°C. The polymerization pressure is sufficient in the range of 1 to
31 60 atmospheres. Adjustment of the molecular weight of the polymer to
32 be obtained is attained by causing the polymerization to proceed in
33 the presence of hydrogen or other known molecular weight adjusting
34 agents. The amount of the other olefin with which the olefin is
35 copolymerized generally is not allowed to exceed 30% by weight and
36 preferably is selected in the range of 0.3 to 15% by weight. The
37 polymerization by the catalyst system of this invention can be carried

1 out continuously or batchwise under those conditions which are
2 generally adopted for the purpose of polymerization. The copoly-
3 merization may be performed in one step or in two or more split
4 steps.

5 Effect of the Invention

6 The catalyst component of the present invention functions
7 effectively as a catalyst for the production of a polyolefin,
8 particularly isotactic polypropylene, a random copolymer of ethylene
9 and propylene, and a block copolymer of ethylene and propylene.

10 The polymerization catalyst using the catalyst component of
11 the present invention possesses high polymerization activity and high
12 stereoregularity and permits the high polymerization activity to be
13 retained long during the course of the polymerization. The olefin
14 polymer powder consequently obtained has high bulk density. The
15 polymer powder abounds with fluidity.

16 EXAMPLE

17 The present invention will be described more specifically
18 below with reference to working examples and applied examples. The
19 examples are for purposes of illustrating the invention and should not
20 be interpreted as a limitation of the invention. The percents (%)
21 mentioned in the working examples and the applied examples are per-
22 cents by weight unless otherwise specified.

23 The heptane insolubles content (hereinafter referred to as
24 "HI") which shows the proportion of crystalline polymer to the whole
25 of a given polymer represents the residue after 6 hours extraction of
26 the polymer with boiling n-heptane in an improved version of Soxhlet
27 extractor. The melt flow rate (MFR) represents the value determined
28 in accordance with ASTM D-1238. The bulk density represents the value
29 determined by the method A defined in ASTM D-1895-69.

30 EXAMPLE 1

31 Contact of Silicon Oxide with n-Butylethyl Magnesium

32 A flask having an inner volume of 200 ml and provided with a
33 dropping funnel and a stirrer has its interior air displaced with
34 nitrogen gas. In the flask, 5 g of silicon oxide (product of Davison
35 Corp. having a specific surface area of $302 \text{ m}^2/\text{g}$, a pore volume of
36 $1.54 \text{ cm}^3/\text{g}$, and an average pore radius of 204 \AA and marketed under
37 the trademark designation of G-952)(hereinafter referred to as
38 " SiO_2 ") fired under a flow of nitrogen gas at 200°C for two hours

1 and further at 700°C for five hours and 20 ml of n-heptane were
2 placed. The compounds so placed and 20 ml of a 20% n-heptane solution
3 of n-butylethyl magnesium (hereinafter referred to as "BEM") (the
4 solution in the amount of 26.8 mmol as BEM) added thereto were stirred
5 at 90°C for two hours. The supernatant consequently formed was
6 removed by decantation and the solid was washed with 50 ml of
7 n-heptane at room temperature and the supernatant formed again was
8 removed by decantation. The washing treatment with n-heptane was
9 repreated four more times.

10 Contact with 2,2,2-trichloroethanol

11 The solid product issuing from the last washing treatment was
12 suspended in 20 ml of n-heptane. Into the resultant suspension, a
13 solution of 9.6 g (64 mmols) of 2,2,2-trichloroethanol in 10 ml of
14 n-heptane was added dropwise through the dropping funnel at 0°C over a
15 period of 30 minutes. The suspension and the added solution were
16 stirred at 0°C for one hour, heated to 80°C over a period of one hour
17 and again stirred at 80°C for one hour. After the completion of the
18 reaction, the reaction mixture at room temperature was washed twice
19 with 50 ml of n-heptane and three times with 50 ml of toluene. The
20 solid consequently obtained (solid component I), by analysis, was
21 found to contain 49.5% of SiO_2 , 3.8% of magnesium, and 33.5% of
22 chlorine. This solid was found to have a specific surface area of 255
23 m^2/g and a pore volume of $0.79 \text{ cm}^2/\text{g}$.

24 Contact with d-n-butyl phthalate and titanium tetrachloride

25 The solid component I obtained in the preceding procedure and
26 20 ml of toluene and 0.6 g of di-n-butyl phthalate added thereto were
27 heated for reaction at 50°C for two hours. Then, the reaction mixture
28 and 30 ml of titanium tetrachloride added thereto were heated for
29 reaction at 90°C for two hours. The solid substance obtained by this
30 reaction was washed at room temperature eight times with 50 ml of
31 n-hexane. It was then dried under a vacuum at room temperature for
32 one hour. Consequently, 7.5 g of a catalyst component was obtained.
33 This catalyst component was found to have a specific surface area of
34 $285 \text{ m}^2/\text{g}$ and a pore volume of $0.87 \text{ cm}^3/\text{g}$. This catalyst component
35 was found to contain 55.9% of SiO_2 , 4.3% of magnesium, 16.3% of
36 chlorine, and 3.1% of titanium.

37 EXAMPLE 2

38 The solid substance formed after contact with titanium

1 tetrachloride in the procedure of Example 1 was separated. This solid
2 substance and 30 ml of titanium tetrachloride added thereto were
3 heated for reaction at 90°C for two hours. The solid substance
4 consequently formed was treated in the same way as in Example 1, to
5 afford a catalyst component having a titanium content of 2.8%.

6 EXAMPLE 3

7 The reaction mixture formed after contact with titanium
8 tetrachloride in the procedure of Example 1 was decanted to expel the
9 supernatant. The solid substance which remained was cleaned in 50 ml
10 of toluene at 90°C for 15 minutes. The washing treatment with toluene
11 was repeated. The washed solid substance and 20 ml of toluene, and 30
12 ml of titanium tetrachloride added thereto were heated for reaction at
13 90°C for two hours. The resultant reaction mixture was washed with
14 n-hexane and dried in the same way as in Example 1, to afford 7.4 g of
15 a catalyst component. This catalyst component was found to have a
16 specific surface area of 279 m^2/g and a pore volume of 0.90 m^3/g .
17 It was found to contain 56.5% of SiO_2 , 4.4 g of magnesium, 15.1% of
18 chloride, and 2.4% of titanium.

19 EXAMPLE 4

20 The procedure of Example 3 was repeated, except that the
21 temperature of contact with titanium tetrachloride was changed from
22 90°C to 120°C. Consequently, there was prepared a catalyst component
23 having a titanium content of 2.1%.

24 EXAMPLE 5

25 The procedure of Example 3 was repeated, except that in the
26 contact of di-n-butyl phthalate and titanium tetrachloride, these two
27 compounds were added at the same time for reaction. Consequently,
28 there was prepared a catalyst component having a titanium content of
29 2.5%.

30 EXAMPLE 6

31 The procedure of Example 3 was repeated, except that in the
32 contact of di-n-butyl phthalate and titanium tetrachloride, 30 ml of
33 titanium chloride was added and abruptly heated to 90°C while under
34 stirring, 0.6 g of di-n-butyl phthalate was added subsequently and
35 heated for reaction at 90°C for two hours. Consequently, there was
36 prepared a catalyst component having a titanium content of 2.4%.

37 EXAMPLE 7

38 The solid component I obtained in the procedure of Example 1

1 and 50 ml of titanium tetrachloride added thereto were stirred and
2 heated suddenly to 90°C. The resultant mixture and 0.6 g of di-n-
3 butyl phthalate added thereto were heated for reaction at 90°C for two
4 hours. After completion of the reaction, the supernatant was removed
5 and the residue and 50 ml of titanium tetrachloride added thereto were
6 heated for reaction at 90°C for two hours. The resultant reaction
7 mixture was washed and dried by following the procedure of Example 1,
8 to afford a catalyst component having a titanium content of 3.3%.

9 EXAMPLE 8

10 In the procedure of Example 7, between the two split steps of
11 contact with titanium tetrachloride, the reaction mixture was washed
12 twice with 50 ml of titanium tetrachloride at 90°C for 15 minutes.
13 The reaction mixture was washed and dried by following the procedure
14 of Example 1. Consequently, there was prepared a catalyst component
15 having a titanium content of 3.0%.

16 EXAMPLES 9-11

17 The procedure of Example 3 was followed, except that in the
18 contact of di-n-butyl phthalate and titanium tetrachloride, xylene
19 (Example 9), n-heptane (Example 10), and 1,2-dichloroethane (Example
20 11) were severally used as an inactive medium in the place of
21 toluene. Consequently, there were prepared catalyst components having
22 titanium contents of 2.2% (Example 9), 3.5% (Example 10), and 2.8%
23 (Example 11).

24 EXAMPLES 12-14

25 During the course of contact with di-n-butyl phthalate and
26 titanium tetrachloride in the procedure of Example 3, the reaction
27 mixture resulting from the first step of contact with titanium tetra-
28 chloride was freed of the supernatant. The residue and 50 ml of
29 toluene and 3 g of silicon tetrachloride (Example 12), 3 g of aluminum
30 trichloride (Example 13), or 3 g of hexachloroethane (Example 14)
31 added thereto were heated for reaction at 60°C for one hour. The
32 resultant reaction mixture was washed four times with 50 ml of toluene
33 at 60°C. The washed reaction mixture was mixed with 20 ml of toluene
34 and 30 ml of titanium tetrachloride to undergo the second reaction
35 with titanium tetrachloride. The reaction mixture consequently
36 obtained was washed and dried in the same way as in Example 1.
37 Consequently, there were produced catalyst components having titanium
38 contents of 2.1% (Example 12), 2.7% (Example 13), and 2.3% (Example

1 14) respectively.

2 EXAMPLES 15 and 16

3 A solid substance was obtained by effecting the reaction of
 4 the solid substance I with titanium tetrachloride and di-n-butyl
 5 phthalate in the same way as in Example 3. This solid substance was
 6 washed eight times with n-hexane similarly to Example 1. The washed
 7 solid substance was converted by addition of n-hexane into a slurry
 8 (4.5 g of solid substance and 6.8 g of n-hexane). The slurry was held
 9 in contact with 1.1 g of hexachloroethane and 100 ml of n-hexane
 10 (Example 15), 100 ml 1,2-dichloro-ethane (Example 16) at 50°C for 30
 11 minutes. The solid substance consequently obtained was separated by
 12 filtration at 50°C, washed with 100 ml of n-hexane at room
 13 temperature, dried under a vacuum for one hour. Consequently, there
 14 were prepared catalyst components having titanium contents of 1.6%
 15 (Example 15) and 1.4% (Example 16) respectively.

16 EXAMPLES 17-20

17 Catalyst components having titanium contents shown below in
 18 Table I were prepared by following the procedure of Example 3, except
 19 that varying metal oxides indicated below were used in the place of
 20 SiO_2 .

21 TABLE I

22	23	Example	Metal Oxide	Firing Conditions	Titanium Content (%)
24	17		Al_2O_3	200°C/2 hours 700°C/5 hours	3.5
25	18		$(\text{MgO})_2(\text{SiO}_2)_3$	200°C/2 hours 500°C/5 hours	2.5
26	19		Mixture of 1 kg of SiO_2 and 100 g of Al_2O_3	200°C/2 hours 700°C/5 hours	2.3
27	20		Mixture of 1 kg of SiO_2 and 20 g of CrO_3	200°C/2 hours 700°C/5 hours	1.9

32 EXAMPLES 21-23

33 Catalyst components having titanium contents indicated below
 34 were prepared by following the procedure of Example 3, except that
 35 varying magnesium compounds indicated below in Table II were used in
 36 the place of BEM.

1

TABLE II

2

3 Example

4

Organic Mg

5

6 Titanium
7 Content (%)

8

9 21 Di-n-hexyl magnesium (product of Texas Alkyls

10 2.5

11

12 Corp., marketed under trademark designation
13 of MAGALA[®] DNHM)

14

15 22 Di-n-butyl magnesium (0.5 mol)-triethyl

16 2.4

17

18 aluminum (1 mol) complex (product of Texas

19

1 Alkyls Corp., marketed under trademark

2

2 designation of MAGALA[®] 0.5E)

3

3 23 Di-n-butyl magnesium (7.5 mols)-triethyl

4 2.5

4

5 aluminum (1 mol) complex product of Texas

6

7 Alkyls Corp., marketed under trademark

8

9 designation MAGALA[®] 7.5E)

10

11 EXAMPLES 24-42

12

13 Catalyst components having titanium contents indicated below
14 in Table III were prepared by following the procedure of Example 3,
15 except that varying halogen-containing alcohols indicated below in
16 Table III were used in the place of 2,2,2-trichloroethanol.

TABLE III

			Titanium Content (%)
	<u>Example</u>	<u>Halogen-Containing Alcohol</u>	
4	24	1,1,1-Trichloro-2-propanol	2.3
5	25	B,B,B-Trichloro-tert-butanol	2.6
6	26	2,2-Dichloroethanol	2.8
7	27	1,3-Dichloro-2-propanol	2.7
8	28	2-Chloroethanol	2.3
9	29	4-Chloro-1-butanol	2.2
10	30	6-Chloro-1-hexanol	2.6
11	31	p-Chlorophenol	2.9
12	32	4-Chloro-o-cresol	2.7
13	33	2,4,6-Trichlorophenol	2.4
14	34	Tetrachlorohydroquinone	2.2
15	35	1-Bromo-2-butanol	2.6
16	36	1,3-Dibromo-2-propanol	2.5
17	37	p-Bromophenol	2.3
18	38	2,4,6-Tribromophenol	2.3
19	39	p-Iodophenol	2.7
20	40	2,4,6-Triiodophenol	2.5
21	41	2,2,2-Trifluoroethanol	2.9
22	42	p-Fluorophenol	2.2

EXAMPLES 43-67

Catalyst components having titanium contents shown below in Table IV were obtained by following the procedure of Example 3, except that varying electron-donating compounds indicated below in Table IV were used in the place of di-n-butyl phthalate during the contact with the solid component I.

1

2

TABLE IV

3	Example	Electron-Donating Compound	Titanium Content (%)
4	43	Ethyl benzoate	2.3
5	44	Diisobutyl phthalate	2.1
6	45	Phthalic anhydride	2.4
7	46	Phthalic acid dichloride	2.7
8	47	Phthalic acid n-butyl chloride	2.5
9	48	Mono-n-butyl phthalate	2.4
10	49	Benzoic anhydride	2.2
11	50	Benzoyl chloride	2.6
12	51	Ethyl cinnamate	2.4
13	52	Ethyl cyclohexane carboxylate	2.5
14	53	Tartaric acid	2.8
15	54	Di-n-butyl tartrate	2.4
16	55	Isobutyl methacrylate	2.3
17	56	Phthalic acid	2.1
18	57	Benzoic acid	3.0
19	58	Di-n-butyl maleate	3.2
20	59	Diisobutyl sebacate	2.8
21	60	Tri-n-butyl trimellitate	2.2
22	61	Ethanol	2.3
23	62	Isobutanol	2.0
24	63	2-Ethylhexanol	2.3
25	64	p-Cresol	2.1
26	65	Diethyl ether	2.0
27	66	Di-n-butyl ether	2.2
28	67	Diphenyl ether	2.5

1 EXAMPLE 682 Contact of Silicon Oxide and 2,2,2-Trichloroethanol

3 A flask having an inner volume of 200 ml and provided with a
4 dropping funnel and a stirrer had its interior air displaced with
5 nitrogen gas. In this flask, 5 g of the same SiO_2 as used in
6 Example 1, 40 ml of n-heptane, and 12 g of 2,2,2-trichloroethanol
7 added thereto were stirred for contact at 90°C for two hours. After
8 completion of the reaction, the reaction mixture was washed three
9 times with 50 ml of n-heptane and decanted at room temperature.

10 Contact with n-butylethyl magnesium

11 The solid substance obtained in the foregoing procedure was
12 suspended in 20 ml of n-heptane. To the resultant suspension, 11 ml
13 of the same BEM solution as used in Example 1 was added dropwise
14 through the dropping funnel at 0°C over a period of 30 minutes. The
15 resultant mixture was stirred at 0°C for one hour, heated to 80°C over
16 a period of one hour, and stirred at 80°C for one hour. After comple-
17 tion of the reaction, the reaction mixture was washed twice with 50 ml
18 of n-heptane and three times with 50 ml of toluene.

19 Contact with di-n-butyl phthalate and titanium tetrachloride

20 By following the procedure of Example 3, except that the
21 solid component obtained in the preceding procedure was used instead
22 in the contact with the di-n-butyl phthalate and titanium
23 tetrachloride, there was obtained 7.8 g of a catalyst component having
24 a titanium content of 2.5%.

25 EXAMPLE 6926 Contact of Silicon Oxide and 2,2,2-Trichloroethanol

27 In a mill pot, 10 g of the same SiO_2 as used in Example 1
28 and 4.4 g of 2,2,2-trichloroethanol were subjected to a crushing
29 treatment for 24 hours.

30 Contact with n-Butylethyl Magnesium

31 A flask having an inner volume of 200 ml and provided with a
32 dropping funnel and a stirrer had its interior air displaced with
33 nitrogen gas. In the flask, 6 g of the solid substance obtained in
34 the preceding procedure and comminuted and 40 ml of n-heptane were
35 placed. Then, 9 ml of the same BEM solution as used in Example 1 was
36 added thereto dropwise through the dropping funnel at 0°C over a
37 period of 30 minutes. The resultant reaction mixture was thereafter
38 treated in the same way as in Example 68 to obtain a solid component.

1 Contact with di-n-Butyl Phthalate and Titanium Tetrachloride

2 By following the procedure of Example 3, except that the
3 solid component obtained in the preceding procedure was used instead
4 in the contact with di-n-butyl phthalate and titanium tetrachloride,
5 there was obtained 8.1 g of a catalyst component having a titanium
6 content of 2.3%.

7 EXAMPLE 708 Contact of 2,2,2-trichloroethanol and n-butylethyl magnesium

9 A flask having an inner volume of 200 ml and provided with a
10 dropping funnel and a stirrer had the interior air displaced with
11 nitrogen gas. In the flask, 5 g of 2,2,2-trichloroethanol and 40 ml
12 of n-heptanol were kept at 0°C. Then, 12.5 ml of the same BEM
13 solution as used in Example 1 was added dropwise at 0°C over a period
14 of 30 minutes. The contents of the flask were stirred at 0°C for one
15 hour, then heated to 80°C over a period of one hour, and then stirred
16 at 80°C for one hour. After completion of the reaction, the reaction
17 mixture was washed three times with 50 ml of n-heptane at room
18 temperature and then dried under a vacuum at room temperature for one
19 hour. Consequently, there was obtained a solid reaction product.

20 Contact with silicon oxide

21 In a mill pot, 5 g of the solid reaction product obtained in
22 the preceding procedure and 8 g of the same SiO₂ as used in Example
23 1 were subjected to a comminution treatment for 24 hours.

24 Contact with di-n-butyl phthalate and titanium tetrachloride

25 By following the procedure of Example 3, except that 6 g of
26 the comminuted solid substance obtained in the preceding procedure was
27 used instead in the contact with di-n-butyl phthalate and titanium
28 tetrachloride, there was obtained 6.8 g of a catalyst component having
29 a titanium content of 2.5%.

30 EXAMPLE 7131 Contact of Silicon Oxide, n-Butylethyl Magnesium, and
32 2,2,2-Trichloroethanol

33 A flask having an inner volume of 200 ml and provided with a
34 dropping funnel and a stirrer had its interior air displaced with
35 nitrogen gas. In the flask, 5 g of the same SiO₂ as used in Example
36 1 and 20 ml of n-heptane were placed. Then 30 ml of the same BEM
37 solution as used in Example 1 was added and subsequently 12 g of
38 2,2,2-trichloroethanol was added dropwise thereto at 0°C over a period

1 of 30 minutes. The resultant mixture was stirred at 0°C for one hour,
2 heated to 80°C over a period of one hour, and stirred at 80°C for one
3 hour. After completion of the reaction, the reaction mixture was
4 washed twice with 50 ml of n-heptane and three times with 50 ml of
5 toluene at room temperature, to obtain a solid component.

6 Contact with di-n-butyl phthalate and titanium tetrachloride

7 By following the procedure of Example 3, except that the
8 solid component obtained in the preceding procedure was used instead
9 in the contact of di-n-butyl phthalate and titanium tetrachloride,
10 there was obtained 7.5 g of catalyst component having a titanium
11 content of 2.6%.

12 APPLIED EXAMPLE 1

13 In a stainless steel autoclave having an inner volume of 1.5
14 liters and provided with a stirrer, a reaction mixture obtained by
15 mixing 30.3 mg of the catalyst component prepared by the procedure of
16 Example 1, 0.97 ml of a solution containing 1 mol of triethyl aluminum
17 (hereinafter referred to as "TEAL") per liter of n-heptane, and 0.97
18 ml of a solution containing 0.1 mol of phenyl triethoxy silane
19 (hereinafter referred to as "PES") per liter of n-heptane and allowing
20 the resultant mixture to stand for five minutes was placed under a
21 blanket of nitrogen gas. Then, 0.1 liter of hydrogen gas as a
22 molecular weight regulator and 1 liter of liquefied propylene were
23 introduced therein under pressure. The reaction system was heated to
24 70°C to effect polymerization of propylene for one hour. After
25 completion of the polymerization, the unaltered propylene was purged
26 to produce 105 g of white polypropylene powder having 97.6% of HI, 4.7
27 of MFR, and 0.42 g/cm^3 of bulk density [Kc (amount of produced
28 polymer in g per g of catalyst component) = 3,500 and Kt (amount of
29 produced polymer in kg per g of titanium in catalyst component) = 113].

30 APPLIED EXAMPLES 2-71

31 Polymerization of propylene was carried out by following the
32 procedure of Applied Example 1, except that the catalyst components
33 obtained in Examples 2-71 were severally used. The results are shown
34 in Table VI. The polypropylene powder obtained in Applied Example 3
35 was tested for particle diameter distribution. The results are shown
36 in Table V below.

1

2 Particle diameter (μm)

3 Less than 149
 4 149 - 250
 5 250 - 350
 6 350 - 420
 7 420 - 590
 8 590 - 840
 9 840 - 1,000
 10 1,000 - 1,680
 11 Exceeding 1,680

TABLE V

Proportion of distribution (%)

0
 0.1
 2.3
 5.9
 24.9
 42.3
 12.8
 11.6
 0.1

12

TABLE VI

13

14	Applied Example	Catalyst Component	Kc (g/g Cat)	Kt (kg/g Ti)	HI (%)	MFR (g/10 min)	Bulk Density (g/cm ³)
15	2	Example 2	3,200	114	97.5	4.5	0.42
16	3	" 3	4,300	179	98.1	4.7	0.44
17	4	" 4	3,900	186	98.0	5.1	0.43
18	5	" 5	3,900	156	97.9	4.0	0.43
19	6	" 6	4,300	179	98.4	3.9	0.45
20	7	" 7	3,100	94	97.7	5.5	0.43
21	8	" 8	3,600	120	98.0	5.0	0.44
22	9	" 9	4,000	182	98.0	4.2	0.43
23	10	" 10	3,600	103	97.9	6.2	0.40
24	11	" 11	3,700	132	97.5	5.8	0.42
25	12	" 12	3,600	171	97.8	4.9	0.41
26	13	" 13	3,900	144	98.2	6.0	0.43
27	14	" 14	3,700	161	98.0	4.9	0.42
28	15	" 15	3,200	200	98.2	5.4	0.44
29	16	" 16	3,400	243	98.3	5.9	0.45
30	17	" 17	3,100	89	97.8	4.5	0.43
31	18	" 18	2,800	112	97.3	4.8	0.41
32	19	" 19	2,600	113	97.2	5.3	0.40
33	20	" 20	2,900	153	97.6	5.8	0.41
34	21	" 21	3,900	156	97.8	4.3	0.44
35	22	" 22	3,600	150	97.6	6.2	0.42
36	23	" 23	3,500	140	97.5	5.8	0.43
37	24	" 24	3,900	170	97.9	4.3	0.44

1

TABLE VI, (cont.)

2

3	4	Applied Example	Catalyst Component	Kc (g/g Cat)	Kt (kg/g Ti)	HI (%)	MFR (g/10 min)	Bulk Density (g/cm ³)
5	25	Example 25		4,100	158	98.0	4.9	0.43
6	26	" 26		3,600	129	97.7	5.6	0.43
7	27	" 27		2,900	107	97.5	5.3	0.43
8	28	" 28		3,200	139	97.6	6.1	0.43
9	29	" 29		3,200	145	97.4	5.6	0.42
10	30	" 30		2,900	112	97.3	6.7	0.43
11	31	" 31		3,600	124	97.7	5.4	0.43
12	32	" 32		3,300	122	97.8	4.8	0.41
13	33	" 33		3,700	154	97.6	6.2	0.42
14	34	" 34		2,700	123	97.6	6.3	0.43
15	35	" 35		2,500	96	97.4	7.1	0.42
16	36	" 36		2,800	112	97.2	5.8	0.41
17	37	" 37		3,100	135	97.1	6.6	0.43
18	38	" 38		2,900	126	97.3	5.5	0.43
19	39	" 39		2,600	96	97.0	4.6	0.42
20	40	" 40		2,500	100	97.4	7.2	0.41
21	41	" 41		3,100	107	97.3	6.8	0.43
22	42	" 42		2,600	118	97.3	6.3	0.42
23	43	" 43		3,000	130	97.9	3.8	0.43
24	44	" 44		3,800	181	98.2	4.0	0.43
25	45	" 45		3,200	133	98.0	4.6	0.40
26	46	" 46		3,500	130	98.1	4.2	0.40
27	47	" 47		3,100	124	98.0	4.0	0.42
28	48	" 48		3,300	138	97.9	5.1	0.41
29	49	" 49		2,900	132	97.9	5.8	0.40
30	50	" 50		2,900	112	97.8	4.0	0.40
31	51	" 51		2,700	113	97.6	4.6	0.38
32	52	" 52		2,900	116	97.8	4.7	0.39
33	53	" 53		2,800	100	97.5	6.1	0.40
34	54	" 54		2,900	121	97.6	4.0	0.40
35	55	" 55		3,100	135	97.6	6.8	0.41
36	56	" 56		3,000	143	97.8	4.2	0.40
37	57	" 57		3,000	100	97.5	4.0	0.40
38	58	" 58		2,900	91	97.6	5.8	0.41

1 TABLE VI, (cont.)
2

3	4	Applied Example	Catalyst Component	Kc (g/g Cat)	Kt (kg/g Ti)	HI (%)	MFR (g/10 min)	Bulk Density (g/cm ³)
5	59	Example 59		3,000	107	97.9	5.2	0.40
6	60	" 60		3,200	145	98.1	4.1	0.43
7	61	" 61		3,000	130	98.0	5.2	0.41
8	62	" 62		2,900	145	97.9	4.8	0.39
9	63	" 63		3,000	130	98.0	4.8	0.41
10	64	" 64		3,100	148	98.0	5.2	0.40
11	65	" 65		2,800	140	97.4	6.8	0.38
12	66	" 66		2,900	132	97.6	6.5	0.39
13	67	" 67		2,900	116	97.6	6.0	0.39
14	68	" 68		4,000	160	98.1	4.1	0.42
15	69	" 69		3,900	170	98.0	3.8	0.38
16	70	" 70		3,900	156	98.2	4.5	0.38
17	71	" 71		3,800	146	97.9	4.4	0.40

18 APPLIED EXAMPLE 7219 Gaseous-phase Polymerization of Propylene

20 In an autoclave having an inner volume of 5 liters and
 21 provided with a stirrer, 150 g of polypropylene powder dried in
 22 advance under a flow of nitrogen gas at 90°C for four hours was
 23 placed. To this autoclave, with the stirrer thereof operated at 150
 24 rpm, the same catalyst component as prepared in Example 3 was fed at a
 25 rate of 50 mg/hr, TEAL at a rate of 0.7 mmol/hr, PES at a rate of 0.05
 26 mmol/hr, propylene at a rate of 130 g/hr, and hydrogen gas at a rate
 27 of 15 ml/hr for continuous polymerization of propylene under the
 28 conditions of 70°C of temperature and 20 kg/cm² of pressure, with
 29 the product of polymerization continuously withdrawn from the
 30 autoclave. Consequently, there was obtained polypropylene powder at a
 31 rate of 90 g/hr. The polymer so produced was found to have an MFR of
 32 5.2 g/10 min and an HI of 96.8%.

33 APPLIED EXAMPLE 7334 Block Copolymerization of Propylene

35 In an autoclave having an inner volume of 1.5 liters and
 36 provided with a stirrer, a reaction mixture obtained by mixing 30.0 mg
 37 of the catalyst component prepared by the procedure of Example 3, 0.75
 38 ml of n-heptane solution of TEAL (1 mol/liter), and 0.75 ml of

1 n-heptane solution of PES (0.1 mol/liter) and allowing the resultant
2 mixture to stand for five minutes was placed under a blanket of
3 nitrogen gas. Then, 100 ml of hydrogen gas and 1 liter of liquefied
4 propylene were introduced therein under pressure. The reaction system
5 consequently formed was heated to 70°C to effect homopolymerization of
6 propylene for one hour. In an experiment of polymerization performed
7 parallelly under the same conditions, the polypropylene obtained was
8 found to have a HI of 98.1%. After completion of the polymerization,
9 the unaltered propylene was purged and the interior of the autoclave
10 was displaced with nitrogen gas. Then, a mixed gas of ethylene and
11 propylene [ethylene/propylene = 1.5 (by mol ratio)] was introduced at
12 such a rate as to keep the monomer gas pressure at 1.5 atmospheres.
13 Under these conditions, copolymerization was effected at 70°C for
14 three hours. After completion of the polymerization, the unaltered
15 mixed gas was discharged. Consequently, there was obtained 175 g of
16 block copolymer of propylene.

17 The proportion of the copolymer fraction calculated based on
18 the consumed amount of the mixed gas and the total amount of polymer
19 was found to be 26.3% and the ethylene content in the total polymer
20 was found by infrared spectral analysis to be 12.6%. Thus, the
21 ethylene content in the copolymer fraction is found by calculation to
22 have been 48%. The amount of the homopolymer of propylene per g of
23 the catalyst component found based on the amount of the total polymer
24 and the consumed amount of the mixed gas was found to be 4,300 g and
25 the amount of the copolymer fraction formed to be 1,530 g. The block
26 copolymer so produced was found to have a MFR of 2.9 g/10 min and a
27 bulk density of 0.44 g/cm³. The polymer particles were free from
28 cohesion and showed absolutely no sign of fouling in the autoclave.

29 APPLIED EXAMPLE 74

30 Random Copolymerization of Propylene and Ethylene

31 During the polymerization of propylene in the procedure of
32 Applied Example 1, 0.6 g of ethylene was introduced under pressure
33 into the autoclave six times at intervals of 10 minutes to effect
34 random copolymerization of propylene and ethylene. After completion
35 of the polymerization, the unaltered monomers were discharged from the
36 polymerization system. Consequently, there was obtained 136 g of a
37 random copolymer of propylene and ethylene. The ethylene content in
38 the produced copolymer was found by infrared spectral analysis to be

1 2.7%. The amount of the copolymer formed per 1 g of the catalyst
2 component was 4,500 g. The produced copolymer was found to have a MFR
3 of 12.4 g/10 min and a bulk density of 0.43 g/cm³.

4 APPLIED EXAMPLE 75

5 Polymerization of 1-Butene

6 By following the procedure of Applied Example 1, except using
7 205 mg of the catalyst component obtained in Example 3, 400 ml of
8 isobutane as a medium, and 400 ml of 1-butene (liquid) in the place of
9 liquefied propylene and carrying out the polymerization under the
10 conditions of 40°C of temperature and five hours of duration, 1-butene
11 was polymerized. Consequently, there was obtained 307.3 g of powdery
12 poly-1-butene. The value, Kc, was found to be 1,500 g/g of catalyst
13 component. The produced polymer was found to have a MFR of 4.1 g/10
14 min, a bulk density of 0.41 g/cm³, and an ether insolubles content
15 (residue after five hours' extraction from boiling diethyl ether). of
16 99.3%.

17 APPLIED EXAMPLE 76

18 Polymerization of 4-methyl-1-pentene

19 By following the procedure of Applied Example 75, except
20 using 230 mg of the catalyst component obtained by Example 3 and 400
21 ml of 4-methyl-1-pentene in the place of 1-butene, 4-methyl-1-pentene
22 was polymerized. Consequently, there was obtained 312.5 g of powdery
23 poly-4-methyl-1-pentene. The value, Kc, was found to be 1,360 g/g of
24 catalyst component. The produced polymer was found to have a MFR of
25 3.5 g/10 min, a bulk density of 0.38 g/cm³, and an ether insolubles
26 content of 98.5%.

CLAIMS:

1. A titanium containing supported catalyst component comprising the product obtained by contacting

(1) a reaction product comprising

(a) an oxide, or a composite oxide, of an element of Group II, or IV of the Periodic Table,

(b) one or more dihydrocarbyl magnesium compounds or a mixture or a complex thereof with an organic compound of aluminium, boron, beryllium, or zinc, and

(c) a halogen-containing alcohol held with

(2) (d) an electron-donating compound and

(e) a di-, tri, or tetravalent titanium compound.

2. The titanium containing supported catalyst component of claim 1, wherein the metal oxide is $\text{SiO}_2/$

3. The titanium containing supported catalyst component of claim 1, or claim 2, wherein the dihydrocarbyl magnesium compound is represented by the general formula RMgR^1 wherein R and R^1 , which can be the same or different, can be an alkyl, cycloalkyl, aryl, or aralkyl group having from 1 to 20 carbon atoms.

4. The titanium containing supported catalyst component of any of claims 1 to 3 wherein the titanium compound is selected from titanium tetrachloride, trichloroethoxy titanium, dichlorodibutoxy titanium and dichlorodiphenoxy titanium.

5. The titanium containing supported catalyst component of any of claims 1 to 4 wherein the electron-donating compound carboxylic esters, carboxylic halides, alcohols, ethers, ketones, amines, amides, nitriles, aldehydes, alcoholates, phosphorous bismuth or antimony compounds bonded to an organic group through carbon or oxygen atoms, phosphamides, theoethers, thioesters, and carbonic sters.

6. The titanium containing supported catalyst component of any of claims 1 to 5 wherein the halogen-containing alcohol is a monohydric or polyhydric alcohol and the halogen atom is chlorine.

7. The titanium containing supported catalyst component of claim 6 wherein the halogen-containing alcohol is a 2,2,2-trichloroethanol.

8. A titanium containing supported catalyst component comprising the product obtained by contacting

(1) a reaction comprising

- (a) SiO_2
- (b) n-butylethyl magnesium, and
- (c) 2,2,2-trichloroethanol, with
- (2) (d) di-n-butylphthalate, and
- (e) titanium tetrachloride.

9. The titanium containing supported catalyst component of any of claims 1 to 8 wherein the reaction product is contacted with the titanium compound at least two times.

10. The titanium containing supported catalyst component of claim 9 wherein the reaction product is contacted with an inactive hydrocarbon, a halide of a hydrocarbon or a metal halide between the titanium compound treatments.

11. A catalyst system for the polymerization of olefins comprising

(A) the titanium containing supported catalyst component of any of claims 1 to 8

and

(B) an organo metallic compound of an element of Groups I to Group III

12. A process for the homopolymerization of an olefin or the copolymerization of an olefin with another olefin, said process comprising polymerizing the olefin(s) in the presence of the catalyst system of claim 11.